TOBACCO-SPECIFIC AND VOLATILE N-NITROSAMINES IN INDOOR AIR OF SMOKER AND NONSMOKER HOMES

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Abstract

The presence of the volatile N-nitrosamine, N-nitrosodimethylamine (NDMA), and the tobacco-specific N-nitrosamines, N-nitrosonornicotine (NNN) and 4-(N-methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK), respirable suspended particles (RSP), ultraviolet particulate matter (UV-PM), oxides of nitrogen (NOx), carbon monoxide (CO), carbon dioxide (CO_2), gas phase (nicotine, 3-ethenylpyridine) and particle phase (solanesol) markers of environmental tobacco smoke (ETS) have been determined in the living room air of homes occupied by smokers and nonsmokers. The mean N-nitrosamine concentrations (in ng/m^3) in homes occupied by smokers were 12.5±6.0 (range 3.3-25.7) NDMA, 0.8±1.2 (not detected {nd}-3.3) NNN and 4.0±4.6 (nd-14.3) NNK. In nonsmoker homes, only NDMA at a concentration of 9.5±0.8 (8.6-10.4) ng/m^3 was detected. Smoking in the home increased the RSP concentration from 85.0±35.4 to 209±164 µg/m^3. Nicotine, 3-ethenylpyridine and solanesol concentrations were below the limit of detection (0.1-0.2 µg/m^3) in nonsmoker homes and present at concentrations of 6.85±9.11, 2.31±2.65 and 2.17±3.17 µg/m^3, respectively, in smoker homes.

Keywords: Nitrosamine, environmental tobacco smoke (ETS), nicotine, TSNA, NDMA, air monitoring

INTRODUCTION

Tobacco-specific N-nitrosamines (TSNA) such as N-nitrosonornicotine (NNN), N-nitrosoanatabine (NAT), N-nitrosoanabasine (NAB) and 4-(N-methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK) are found in cured tobacco and transfer to mainstream and sidestream cigarette smoke during smoking [1,2]. As a result, trace quantities of TSNA have been reported in environmental tobacco smoke (ETS) in bars, restaurants and trains [3], and in a poorly ventilated office where

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extensive smoking occurred [4]. In the present study, N-nitrosamines, respirable suspended particles (RSP), ultraviolet particulate matter (UV-PM), carbon monoxide (CO), carbon dioxide (CO_2), oxides of nitrogen (NOx) and surrogate markers for ETS (solanesol, 3-ethenylpyridine and nicotine) were determined under real-life conditions in the living room air of 5 homes occupied only by nonsmokers and 15 homes occupied by at least one smoker.

MATERIALS AND METHODS

Twenty homes in the city and suburbs of Munich were investigated, five of which had only nonsmoking residents. Air monitoring was performed during the evening with all residents present in the home and no attempt was made to influence the smoking habits of the residents during the sampling sessions.

The sampling apparatus was located close to the center of the living room and installed at the breathing height of a seated person. Real-time CO_2 was determined using a portable infrared monitor (Multiwarn, Dräger AG, Germany). Indoor air was sampled using two portable air sampling systems (Portable Air Sampler, TNO, Division of Technology, Delft, The Netherlands [5]; and PASS, ARJAY Equipment Corp., USA). A time-weighted air sample was collected using a Tedlar (PVF) sampling bag for direct on-line measurement of CO (Carbon Monoxide Analyzer Model 8310; Monitor Labs Inc., USA) and NOx (Nitrogen Oxide Analyzer Model 8840; Monitor Labs Inc., USA). Nicotine [6], 3-ethenylpyridine [7], solanesol [8], RSP and UV-PM [9] were determined according to published methods.

A self-constructed portable air sampling case was used for sampling of TSNA and volatile N-nitrosamines on a Cambridge filter impregnated with 0.1M $KHSO_4$ and a Thermosorb air sampling cartridge (Thermeditec Inc., USA) placed between the Cambridge filter and the air sampling pump operated at a flow rate of 2 l/min. After sampling (0.5 m^3 indoor air), the filter was extracted by 10 min sonification in 50 ml 0.1M citric acid buffer. Nitrosamines were extracted from the citric acid buffer with four 25 ml aliquots of dichloromethane and the combined organic extract dried over anhydrous Na_2SO_4 prior to concentration to 2 ml at ambient temperature. The dichloromethane extract was chromatographed on a short column containing 10 g aluminium oxide and eluted with 25 ml dichloromethane to recover the volatile N-nitrosamine fraction. TSNA were eluted from the column with 25 ml dichloromethane:acetone (4:1 v/v) and concentrated in vacuo at ambient temperature to 100 µl for analysis by gas chromatography using a thermal energy analyzer (GC-TEA) [10]. The Thermosorb cartridge was eluted with 2 ml dichloromethane:methanol (3:1 v/v) and the eluate added to the volatile N-nitrosamine fraction extracted from the Cambridge filter. The combined fractions were concentrated to ca. 2 ml and chromatographed on a short column containing 10 g aluminium oxide using 25 ml of

dichloromethane as the eluant. The dichloromethane eluate was concentrated to a final volume of 200 µl for analysis by GC-TEA [10]. The presence of N-nitrosamines was confirmed by photolysis of the sample at 365 nm and repeat analysis by GC-TEA [11].

RESULTS

The time-integrated living room air concentrations of tobacco smoke constituents and N-nitrosamines are shown in Table 1. The concentrations of surrogate markers for ETS were below the limit of detection (0.1-0.2 µg/m^3) in homes occupied by nonsmokers. In homes occupied by one or more smokers, mean concentrations (µg/m^3) were: 6.85±9.11 (range 0.4-30.4) nicotine, 2.31±2.65 (0.1-7.4), 3-ethenylpyridine and 2.17±3.17 (0.2-12.5) solanesol. The presence of smokers in the home increased the mean concentration of RSP and UV-PM from 85.0±35.4 to 209±164 µg/m^3 and 32.4±6.8 to 92.9±119.9 µg/m^3, respectively. Similar smoking-related increases were found for CO (0.2±0.1 vs 0.8±0.8 ppm) and NOx (0.02±0.005 vs 0.03±0.03 ppm). The mean concentrations of CO_2 (0.08±0.02 and 0.09±0.04%) were almost identical in nonsmoking and smoking homes. The mean N-nitrosamine concentrations (in ng/m^3) were: 12.5±6.0 (3.3-25.7) NDMA, 0.8±1.2 (nd-3.3) NNN and 4.0±4.6 (nd-14.3) NNK in homes occupied by smokers. In homes occupied by nonsmokers, 9.5±0.8 (8.6-10.4) ng/m^3 NDMA was the only N-nitrosamine detected.

DISCUSSION

The levels of surrogate markers for ETS (nicotine, 3-ethenylpyridine and solanesol) confirmed that the homes studied were genuinely occupied by either nonsmokers or families containing smokers. Smoking in the home resulted in an almost 3-fold increase in the concentration of RSP and UV-PM. The mean concentrations for all of the measured indoor air constituents except for CO_2 were significantly ($p<0.001$) higher in homes occupied by smokers.

This is the only reported study in which TSNA have been determined in indoor air with well characterized ETS concentrations. Trace concentrations of 0.8±1.2 ng/m^3 NNN and 4.0±4.6 ng/m^3 NNK were found only in homes occupied by smokers. In previous studies, 7.4±9.1 (nd-22.8) ng/m^3 NNN and 9.5±9.2 (1.4-23.8) ng/m^3 NNK were determined in bars and restaurants by Brunnemann et al. [3], and 2.8±1.6 (nd-6.0) ng/m^3 NNN and 4.9±3.6 (nd-13.5) ng/m^3 NNK in a poorly ventilated office where extensive smoking occurred [4]. Studies by Brunnemann et al. reported only the presence of TSNA in ETS without characterizing the ETS or determining the indoor air quality. In our previous study on ETS in a poorly ventilated office [4], nicotine was determined as a surrogate marker for ETS and indoor air quality assessed by measuring both NOx and

CO. In both our previous study [4] and the current investigation, no correlations existed between any of the surrogate markers for ETS and individual or total N-nitrosamine concentrations in indoor air.

The mean NDMA concentration was slightly higher in homes occupied by smokers (12.5±6.0 ng/m^3) compared to nonsmoking homes (9.5±0.8 ng/m^3). The presence of NDMA in indoor air is not specifically due to ETS since this N-nitrosamine occurs ubiquitously in the environment [12], and in ambient outdoor air where concentrations as high as 90 ng/m^3 have been measured in industrial areas [13].

Our results confirm earlier findings that ETS contains trace amounts of TSNA. In addition, ETS causes a slight elevation in the levels of NDMA in indoor air of households in which smokers are resident. According to several published studies, about 80% of the total ETS exposure of nonsmokers either married to or living with a smoker in the household occurs within the home [14-17]. Compared to the average daily dietary intake of 0.2-0.3 µg NDMA [18] and an estimated total daily dietary intake of 10-100 µg for all N-nitrosamines [19], it is concluded that exposure to N-nitrosamines in ETS does not significantly contribute to the total exogenous daily N-nitrosamine exposure and is also negligible compared to the potential for endogenous nitrosamine formation from nitrosatable secondary amines present in human body fluids [20].

References

1. Hoffmann, D., Adams, J.D., Brunnemann, K.D. and Hecht, S.S.: Assessment of tobacco-specific N-nitrosamines in tobacco products. Cancer Res. 39,2505-2509 (1979)
2. Tricker, A.R., Ditrich, C. and Preussmann, R.: N-Nitroso compounds in cigarette tobacco and their occurrence in mainstream tobacco smoke. Carcinogenesis 12,257-261 (1991)
3. Brunnemann, K.D., Cox, J.E. and Hoffmann, D.: Analysis of tobacco-specific N-nitrosamines in indoor air. Carcinogenesis 13,2415-2418 (1992)
4. Klus, H., Begutter, H., Scherer, G., Tricker, A.R. and Adlkofer, F.: Tobacco-specific and volatile N-nitrosamines in environmental tobacco smoke of offices. Indoor Environ. 1,348-50 (1992)
5. Van der Wal, J.F.: Portable air sampler for measurements in aircraft and public buildings. In: Bieva, C.J., Courtois, Y. and Govaerts, M., eds., Present and future of indoor air quality. Elsevier Science Publisher B.V., Amsterdam. 371-378 (1989)

6. Ogden, M.E.: Gas chromatographic determination of nicotine in environmental tobacco smoke: collaborative study. J. Assoc. Off. Anal. Chem. 72,1002-1006 (1989)
7. Eatough, D.J., Benner, C.L., Tang, H., Landon, V., Richards, G., Caka, F.M., Crawford, J., Lewis, E.A., Hansen, D.L. and Eatough, N.L.: The chemical composition of environmental tobacco smoke. III. Identification of conservative tracers of environmental tobacco smoke. Environ. Int. 15,19-28 (1989)
8. Ogden, M.W. and Maiko K.: Comparison of GC and LC for determining solanesol in environmental tobacco smoke. Liquid Chromatography/Gas Chromatography, 10,459-462 (1990)
9. Conner, J.M., Oldaker, G. and Murphy, J.J.: Method for assessing the contribution of environmental tobacco smoke to respirable suspended particles in indoor air. Environ. Technol. Lett. 11,189-196 (1990)
10. Begutter, H., Klus, H. and Ultsch, L.: Kapillargaschromatographische Bestimmung flüchtiger und tabakspezifischer N-Nitrosamine mittels des Thermal Energy Analyzers. J. Chromatogr. 321,475-479 (1985)
11. Fiddler, W., Doerr, R.C. and Piotrowski, E.G.: Observations on the use of thermal energy analyzer as a specific detector for nitrosamines. In: Walker, E.A., Castegnaro, M., Griciute, L. and Lyle, R.E., eds., Environmental aspects of N-nitroso compounds, IARC Scientific Publications No. 19. International Agency for Research on Cancer, Lyon. 33-39 (1978)
12. Tricker, A.R., Spiegelhalder, B. and Preussmann, R.: Environmental exposure to preformed nitroso compounds. Cancer Surv. 8,251-272 (1989)
13. Akkan, Z., Preussmann, R. and Spiegelhalder, B.: N-Nitrosamines in ambient air of industrial areas in Germany. J. Cancer Res. Clin. Oncol. 117,S14 (1991)
14. Becher, H., Jahn, I., Jöckel, K.H. and Bödeker, W.: Passivrauchen als Gesunheitsrisiko (Ministerium für Arbeit, Gesundheit und Soziales des Landes NRW), Busse Druck, Herford (1987)
15. Haley, N.J., Colosimo, S.G., Axelrad, C.M., Harris, R. and Sepkovic, D.W.: Biochemical validation of self-reported exposure to environmental tobacco smoke. Environ. Res. 49,129-135 (1989)
16. Riboli, E., Preston-Martin, S., Saracci, R., Haley, N.J., Trichopoulos, D., Becher, H., Burch, J.D., Fontham, E.T.H., Gao, Y.-T., Jindal, S.K., Koo, L.C., Le Marchand, L., Segnan, N., Shimizu, H., Stanta, G., Wu-Williams, A.H. and Zatonski, W.: Exposure of nonsmoking women to environmental tobacco smoke: a 10-country collaborative study. Cancer Causes and Control 1,243-252 (1990)

17. Scherer, G., Ruppert, T., Daube, H., Kossien, I., Riedel, K., Tricker, A.R. and Adlkofer, F.: Environmental tobacco smoke (ETS) exposure in homes with and without smokers. This volume (1994)
18. Tricker, A.R., Pfundstein, B., Theobald, E., Preussmann, R. and Spiegelhalder, B.: Mean daily intake of volatile N-nitrosamines from foods and beverages in West Germany in 1989-1990. Food Chem. Toxicol. 11,729-732 (1991)
19. Tricker, A.R. and Preussmann, R.: Carcinogenic N-nitrosamines in the diet: occurrence, formation, mechanisms and carcinogenic potential. Mutation Res. 259,277-289 (1991)
20. Tricker, A.R., Pfundstein, B. and Preussmann, R.: Nitrosatable secondary amines: exogenous and endogenous exposure, and nitrosation in vivo. In: Loeppky, R.N. and Michejda, C., eds., Nitrosamines and related N-nitroso compounds, chemistry and biochemistry. ACS Symposium Series 553, American Chemical Society, Washington DC. 93-101 (1994)

Table 1. Air monitoring in the living room of homes occupied by nonsmokers and smokers

Indoor air component	Nonsmoker home (n=5)		Smoker home (n=15)	
	Mean	Range	Mean	Range
RSP ($\mu g/m^3$)	85.0±35.4	50-137	209±164	69-581
UV-PM ($\mu g/m^3$)	32.4±6.8	2.4-43	92.9±119.9	2-489
Carbon monoxide (ppm)	0.2±0.1	0.1-0.3	0.8±0.8	0.1-3.0
Carbon dioxide (%)	0.08±0.02	0.06-0.11	0.10±0.04	0.04-0.20
NOx (ppm)	0.02±0.005	0.02-0.03	0.03±0.03	0.01-0.12
Nicotine ($\mu g/m^3$)		<0.1 (LOD)[1]	6.85±9.11	0.4-30.4
3-Ethenylpyridine ($\mu g/m^3$)		<0.1 (LOD)	2.31±2.65	0.1-7.4
Solanesol ($\mu g/m^3$)		<0.2 (LOD)	2.17±3.17	0.2-12.5
NDMA (ng/m^3)	9.5±0.8	8.6-10.4	12.5±6.0	3.3-25.7
NNN (ng/m^3)		<0.5 (LOD)	0.8±1.2	0-3.3
NNK (ng/m^3)		<0.5 (LOD)	4.0±4.6	0-14.3
Σ NDMA, NNN, NNK (ng/m^3)	9.5±0.8	8.6-10.4	17.0±9.2	4.4-32.7

[1]LOD, limit of detection.